UNIVERSITI PUTRA MALAYSIA

ACTIVATED CARBONS PREPARED FROM OIL PALM SHELLS: CHARACTERISATIONS AND APPLICATION FOR COLUMN SEPARATION OF HEAVY METALS

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FSAS 2002 42

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of Requirement for the Degree of Master of Science

August 2002

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chairman : Associate Professor Anuar Kassim, Ph.D.

Faculty : Science and Environmental Studies.

Wastes from agricultural products are abundant, suitable to be used as precursor for producing activated carbons. These wastes, instead of causing significant disposal problems, can be turned into by-products for industries by utilizing them for manufacturing activated carbons.

Carbonization and activation processes were done in the Tubular Carbolite Furnace. N_2 gas was flowed for the first 3 hours followed by CO_2 gas for the next 1 hour on the precursor at the constant temperature of 500 °C. For the H_3PO_4 impregnation, 30 grams of the palm shells were impregnated with 15 ml of H_3PO_4 and diluted with 100 ml of distilled water to produce 2.2 M H_3PO_4 solution. For the K_3PO_4, 30 grams of palm shells were impregnated with 9 g of K_3PO_4 and diluted with 100 ml of distilled water to produce 9 % w/w K_3PO_4 solution. For the KOH impregnation, 30 grams of palm shells were impregnated with 9 g of KOH and diluted with 100 ml of

distilled water to produce 9 % w/w KOH solution.

Several physico-chemical characterizations of the internal surface texture and adsorption properties in gas and liquid phase of the prepared activated carbons were performed. Two types of pores, which dominate the activated carbons, are known as mesopores and micropores. The activated carbon prepared by physical method contained more micropore compared to the chemical method in which the latter has significant number of mesopores. The BET surface area of AC H_3PO_4 was the highest, that is, 760 m^2/g, whereas the AC K_3PO_4 had the lowest, which is, 75 m^2/g. Consequently, AC K_3PO_4 has the largest pore diameter, 25 Å and the lowest micropores percentage. This indicates that pore widening had occurred. All activated carbons prepared in this study had the pH level adjusted to pH 5.5.

Column chromatography studies were done using the activated carbons as packing material. The activated carbons were used to adsorb and separate a tri-component system consisting of Pb, Zn, and Fe metal ions, since adsorption capacity analysis using batch method indicated that separation of this system was possible. For AC 7080, AC 4050, AC H_3PO_4 and AC KOH, the elution curves were similar. Zn metal ion was eluted at about pH 2 followed by Pb metal ion at about pH 1 and Fe metal ion at about pH 0. For AC PHY, Pb metal ion was eluted at about pH 2 followed by Zn metal ion at about pH 1 and Fe metal ion at about pH 0. For AC K_3PO_4, Pb metal ion was eluted at about pH 1 followed by Zn and Fe metal ions at about pH 0.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN KARBON AKTIF DARIPADA TEMPURUNG KELAPA SAWIT: PENCIRIAN DAN PENGGUNAAN DALAM TURUS PEMISAHAN UNTUK LOGAM-LOGAM BERAT

Oleh

COLLIN GLEN JOSEPH A/L ANTHONY JOSEPH

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Fakulti : Sains dan Pengajian Alam Sekitar

Sisa daripada hasil pertanian adalah satu sumber yang banyak dan sesuai digunakan sebagai bahan untuk memproses karbon aktif. Sisa ini yang akan menyebabkan masalah pembuangan, boleh dijadikan sebagai hasil sampingan untuk industri dengan menggunakannya sebagai bahan mentah untuk memproses karbon aktif.

Proses pengkarbonan dan pengaktifan telah dilakukan didalam 'Tubular Carbolite Furnace'. Gas N_2 dialirkan untuk 3 jam pertama diikuti oleh gas CO_2 untuk satu jam berikutnya pada suhu tetap, 500 ^{o}C. Dalam impregnasi H_3PO_4, 30 gram tempurung kelapa sawit telah dicampurkan dengan 15 ml H_3PO_4 dan 100 ml air suling untuk menghasilkan kepekatan larutan H_3PO_4 2.2 M. Dalam impregnasi K_3PO_4, 30 gram tempurung kelapa sawit telah dicampurkan dengan 9 gram K_3PO_4 dan 100 ml air suling untuk menghasilkan larutan K_3PO_4 9 % berat/berat. Dalam impregnasi KOH,

30 gram tempurung kelapa sawit telah dicampurkan dengan 9 gram KOH dan 100 ml air suling untuk menghasilkan larutan KOH 9 % berat/berat.

Beberapa pencirian fisiko-kimia terhadap tekstur permukaan luaran, permukaan dalaman dan sifat penjerapan dalam fasa gas dan cecair ke atas karbon aktif yang disediakan telah dilakukan. Terdapat dua jenis liang utama yang mendominasi karbon aktif iaitu liang mikro dan meso. Karbon aktif fizikal mengandungi lebih banyak liang mikro berbanding karbon aktif kimia, yang mempunyai liang meso yang cukup banyak. Luas permukaan BET untuk AC H_3PO_4 adalah tertinggi, iaitu 760 m_2/g, manakala AC K_3PO_4 adalah terendah iaitu sebanyak 75 m^2/g. AC K_3PO_4 mempunyai diameter liang terbesar iaitu 25Å dan peratus liang mikro terendah. Ini membuktikan bahawa pembesaran liang berlaku. Semua karbon aktif dalam kajian ini mempuyai pH 5.5.

Kajian kromatografi turus menggunakan karbon aktif sebagai bahan padatan telah dilakukan. Karbon aktif telah digunakan untuk menjerap dan memisahkan campuran dalam sistem yang mengandungi Pb, Zn dan Fe kerana data muatan jerapan menggunakan kaedah kelompok menunjukkan pemisahan dapat dilakukan. AC 7080, AC 4050, AC H_3PO_4 dan AC KOH mempunyai bentuk keluk elusi yang sama. Ion logam Zn telah dielusi pada pH 2 diikuti dengan ion logam Pb pada pH 1 dan ion logam Fe pada pH 0. Untuk AC PHY, ion logam Pb telah dielusi pada pH 1 diikuti oleh ion logam Zn dan Fe pada pH 0.

ACKNOWLEDGEMENTS

First of all, I would like to thank the Almighty God for His mercy, guidance and patience towards my spiritual growth and walk with Him in these two years. I would also like to express my deepest and warmest sense of thanks and appreciation to my family for which their love, encouragement and support made it possible for me to complete my post-graduate studies in UPM.

I would like to express my sincere appreciation to my honorable project supervisor, Assoc. Prof. Dr. Anuar Kassim, for his assistance, constructive criticisms, advice and guidance throughout the duration of this project. Sincere thanks are also extended to my co-supervisors, Assoc. Prof. Dr. Zulkarnain Zainal, Assoc. Prof. Dr. Mohd. Zobir Hussein, Assoc. Prof. Dr. Md. Jelas Haron and Dr. Abdul Halim Abdullah for their valuable assistance in making this research successful.

I wish to express my gratitude to all the staff of the Chemistry Department, especially En. Kamal and Madam Choo. I am also very grateful for the scholarship awarded to me under Pasca Siswazah Scheme by Universiti Putra Malaysia.

Finally, I would like to take this opportunity to thank my lab mates especially Saravana-kumar and those who had contributed to the success of this research in one way or another.

I certify that an Examination Committee met on 9th August 2002 to conduct the final examination of Collin Glen Joseph on his Master of Science thesis entitled "Activated Carbons Prepared from Oil Palm Shells: Characterisations and Application for Column Separation of Heavy Metals" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the degree of Master of Science. Members of the Supervisory Committee are as follows:

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DECLARATION

I hereby declare that this thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Collin G. Joseph

COLLIN GLEN JOSEPH A/L ANTHONY JOSEPH

Date : 26/9/2002

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LIST OF ABBREVIATION

RAW - Oil palm shells.

AC PHY - Activated carbon prepared by physical activation.

AC H_3PO_4 - Activated carbon prepared by chemical activation using Phosphoric acid.

AC K_3PO_4 - Activated carbon prepared by chemical activation using Potassium Phosphate.

AC KOH - Activated carbon prepared by chemical activation using Potassium Hydroxide.

AC 4050 - Commercial activated carbon.

AC 7080 - Commercial activated carbon.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. It consists principally of carbon (87 to 97 %) but also contains elements such as hydrogen, oxygen, sulphur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture. Activated carbon may also contain various useless mineral substances in quantities of 1 to 20 %. Activated carbon has the ability to adsorb various substances from both gas and liquid phases. It is this ability to arrest different molecules at the inner surface of activated carbon that justifies calling it an adsorbent (Jankowska *et al.*, 1991). The ability of fluid molecules to adhere to the surfaces of solids is a phenomenon known as adsorption (Hassler, 1974).

The pore volume of the activated carbon usually exceeds 0.2 cm^3g^{-1}, the inner specific surface area is generally greater than 400 m^2g^{-1} and the linear dimensions of the pores (i.e. their radii) range from 0.3 to several thousands nanometers (Jankowska *et al.*, 1991).

1.2 History

Hippocrates and his disciples recommended dusting wounds with powdered charcoal in order to remove their unpleasant odour. In 1773, Swedish chemist Karl

Wilhelm Scheele discovered the phenomenon of adsorption of gases on charcoal. In 1785, the Russian academician Lovits from Saints Petersburg found that charcoal, when immersed in tartaric acid solution, decolorizes it by adsorbing the organic contaminants present. In 1794, activated carbon was used as a decolorizing agent for sugar syrup in England. This event initiated research on adsorption from the liquid phase. Russian scientist, Mikhail Tsvet discovered the selectivity of the adsorption process in 1903. Tsvet referred to this process as the adsorptive chromatographic separation of mixtures. In 1900-1901, Ostrejko was granted two patents which opened new prospects for the manufacturing technology of activated carbon. The process of chemical activation of sawdust with zinc chloride was carried out for the first time in 1914 in the Austrian plant in Aussig and also in the dyestuff plant of Bayer. World War 1 accelerated the research in activated carbon because of the introduction of chemical warfare by the Germans. Nikolai Zelinski, a professor of Moscow University, was the first to suggest the use of activated carbon as the adsorption medium in gas masks (Jankowska *et al*., 1991).

1.3 Properties of Activated Carbon

Activated carbon contains a wide range of micropore, the walls of which have surface area that range from 400 to over 1800 m^2/g in various commercial brands. To be effective, activated carbon must have more than just a large surface, it must be selective, that is, to take up and hold molecules of the substance to be removed without disturbing other substances in the system. Activated carbon can meet many of the diverse needs

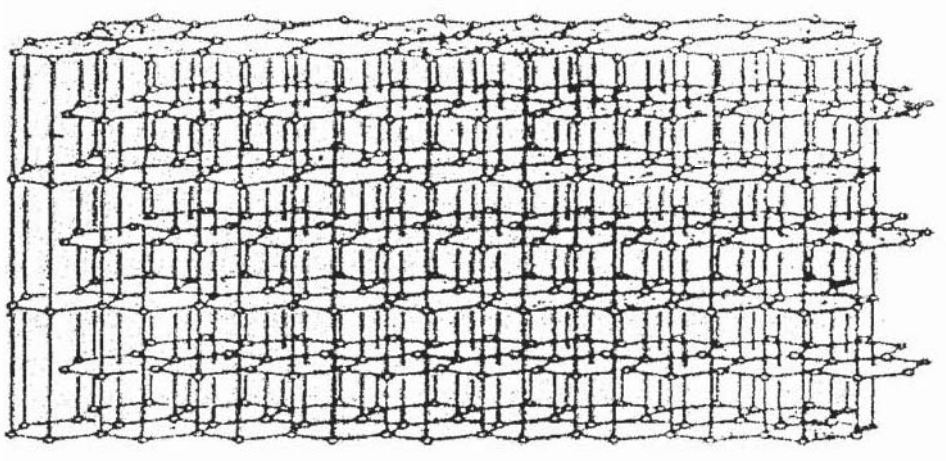
because the adsorptive properties can be developed in various forms by appropriate changes in the manufacturing process (Hassler, 1974).

1.3.1 Physical Structure of Activated Carbon

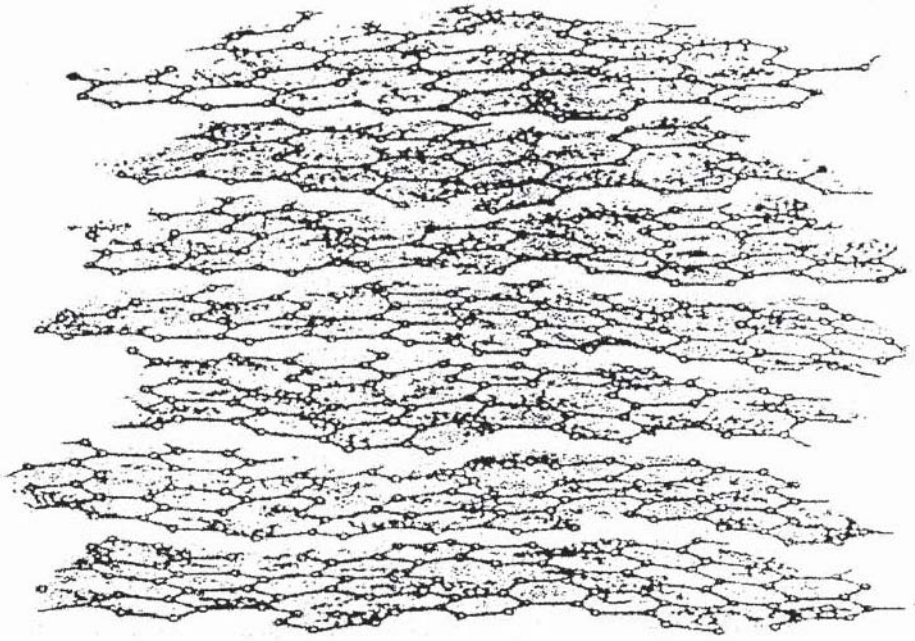
There are two types of carbon structure: a) graphite carbon and b) turbostratic carbon (Figure 1). Activated carbon has turbostratic carbon structure type, having microcrytallites only a few layers in thickness and less than 100 Å in width. Activated carbon owes a large portion of their remarkable adsorption properties to their porous nature. Physical parameters such as porosity can be controlled to some degree to produce carbon suited for special applications. Adsorption of molecules from solution is highly dependent on the porous nature of the activated carbon (Clark and Lykins, 1989).

1.3.2 Chemical Properties

Main element in activated carbon is, of course, carbon with about 87-97 % of the composition. Other elements present are hydrogen, sulphur and nitrogen that are in the precursor or formed during the activation process (Jankowska *et al.*, 1991). These elements are chemically bonded to form functional groups such as carbonyl, carboxylic, phenol, lactone, quinone and ester (Figure 2).

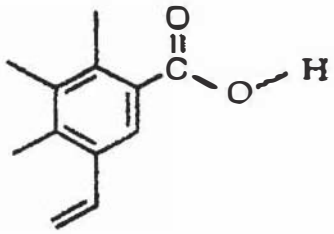


(a)

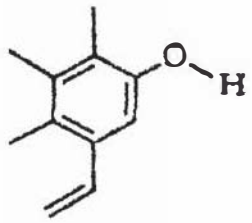


(b)

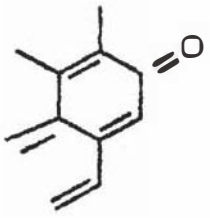
Figure 1: Schematic diagram comparing (a) a three-dimensional graphite lattice with (b) a turbostratic structure (Mattson and Mark, 1971).



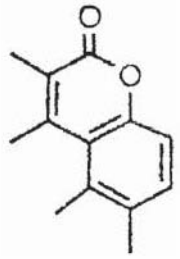
(i) Carboxyl groups



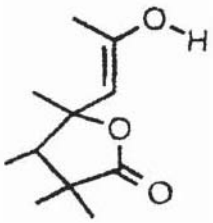
(ii) Phenolic hydroxyl groups



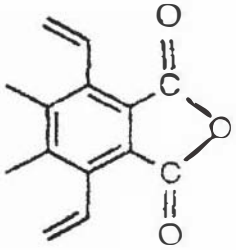
(iii) Quinone-type carbonyl groups



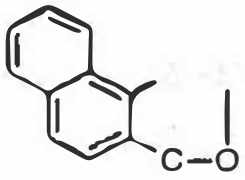
(iv) Ester -like groups



(v) Fluorescein-like lactones



(vi) Carboxylic acid anhydrides



(vii) Cyclic peroxide

Figure 2 : Functional groups present in activated carbon (Jankowska *et al.*, 1991).

Activated carbon also produces ash, about 1-20 %, which decreases during the washing process with water or acid. The main content of ash is carbonate, phosphate and silica (Gerhatz, 1986). The ashes which can be removed by washing the activated carbon with distilled water or mild acid solution will decrease to 0.1-0.2 % (Jankowska *et al.*, 1991). Surface oxide groups can be removed by heat treatment of carbon in an inert atmosphere or under vacuum (Puri, 1962; Puri and Bansal, 1965; Puri, 1966). Evolution of CO_2 is observed at temperature below 600 °C and surface acidity is closely related to the amount of the evolved CO_2. Above 600 °C, the evolving CO_2 produces the basic functional groups on the carbon surface (Jankowska *et al.*, 1991).

1.3.3 Physical Properties

Surface area is the most important physical property of the activated carbon, which affects the adsorption. However, adsorption also depends upon the molecular size of the adsorbate and the pore diameter of the activated carbon. Particle size distribution also plays an important part in the adsorption, because it determines the activated carbon resistance layer to the flow of fluids (Gerhatz, 1986).

1.4 Porosity Structure

Activated carbon has the ability to adsorb well due to its porosity criteria. Dubinin (1966) classified pore to three types according to the sizes.

Table 1: Pore type and diameter.

Pore type	Diameter
micropores	less than 20 Å (2 nm)
mesopores	between 20 and 500 Å (2 and 50 nm)
macropores	more than 500 Å (50 nm)

For micropores, the interaction potential is greater compared to pores that are bigger due to the distance between the smaller walls and the amount that is adsorbed when the relative pressure increases. With mesopores, there is the capillary condensation with histeresis loop effect and for macropores, it is difficult to determine the isotherm because of the relative pressure which is near to one.

For the last few years, the range for the micropore can be divided to smaller size, that is, ultramicropores and supermicropores that falls in the range between ultramicropores and micropores (Gregg and Sing, 1982).

1.5 Elementary Aspects of Adsorption

Atoms and molecules are held together in a solid by cohesive forces that range from strong valence bonds to the weak van der Waals forces of attraction. Molecules at the interior of a solid are completely surrounded, consequently their attractive forces do not cease abruptly at the surface. Instead they tend to extend outward and can capture wandering fluid molecules – a phenomenon that is known as adsorption (Hassler, 1974).